Supporting Information for:

Ordered Silicon Microwire Arrays Grown From Substrates Patterned Using Imprint Lithography And Electrodeposition

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EXPERIMENTAL METHODS

Fabrication of Microimprint Stamps: Microimprint stamps were fabricated by casting two layers of PDMS, each having different gel strengths, onto a reusable master that was made from a Si wafer coated with thermal oxide. The pattern consisted of a square-packed array of 3 μm diameter holes spaced 7 μm from center to center. The oxide thickness, and therefore the height of the stamp features, was 150 nm.

The high gel-strength x-PDMS was made by combining vinylmethylsiloxane copolymer, platinum-divinyltetramethyldisiloxane complex in xylene, vinyl-modified Q silica resin (50% in xylene) and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (all components from Gelest, Inc.).[1] These reagents were mixed for 1 min and defoamed for 1 min (Thinky Conditioning Mixer, Phoenix Equipment, Inc.). The mixture was then degassed in a vacuum chamber for 2 min. Hydride-functional polydimethylsiloxane (50-55% (methylhydrosiloxane) 45-50% (dimethylsiloxane) copolymer) was added as a curing agent, and the components were then mixed and defoamed for 1 min. The mixture was then degassed for 8 min, and the x-PDMS was spin-coated onto the silicon master (which had been treated with trimethylchlorosilane to prevent adhesion) at 500 rpm for 60 s. The thickness of this layer was ~ 26 μm, as determined by contact profilometry (Bruker DektakXT). While the x-PDMS layer was being pre-cured for 10 min at 55˚C, a mixture of 10:1 Sylgard 184 (Dow Corning) PDMS was made by combining

the monomer and curing agent, mixing for 1 min, and defoaming for 5 min. The 10:1 PDMS was then poured over the wafer and degassed for an additional 10 min. The stamp was then cured overnight at 80˚C.

Microimprint Lithography: A degenerately doped, non-photoactive Si(111) wafer (with a resistivity, $\rho < 0.003$ Ω-cm, Addison Engineering, Inc.) was cleaned in buffered HF(aq) for 1 min to remove any native oxide. The wafer was then thoroughly rinsed in 18 MΩ-cm resistivity deionized H_2O. A ~ 150 nm thick layer of sol-gel material (Philips or Filmtronics 11F or 400F) was then spin-coated onto the wafer. The bilayer stamp (which is the same size as the wafer to be patterned) was pressed into the sol-gel, and a glass slide was used to force out any air bubbles trapped between the wafer and the stamp. The stamp and wafer were dried under ambient conditions for 1 h, to allow the solvents to diffuse out through the PDMS stamp and to allow the sol-gel to fully crosslink. The stamp was then carefully peeled away from the wafer.

Electrodeposition of the VLS Catalyst: Before electrodeposition, the sample was then immersed in a dilute (2% by volume) HF(aq) solution to remove any residual sol-gel or native oxide from the patterned regions of the wafer. Control over the duration of this etch allowed for exposure of the conductive silicon substrate at the bottom of the holes, but left a confining SiO_2 layer elsewhere. The wafer was then rinsed with 18 MΩ-cm resistivity deionized H_2O and dried under a stream of N_2(g). A pressed electrochemical cell (**Figure S1**) was used for the electrodeposition, to avoid epoxy or other methods of insulating the backside of the wafer during electrodeposition of the Cu catalyst. An aqueous commercial Cu electrodeposition solution (pH = 9, Copper Primer, Clean Earth Solutions) was used, along with a 99.999% Cu rod as the

counter electrode. Cyclic voltammetry from -0.50 V to -1.50 V at a scan rate of 50 mV s^{-1} was used to determine the optimal potential for potentiostatic deposition (-1.05 V vs. Ag/AgCl). The amount of charge passed was used to control the thickness of the copper within each hole in the patterned sol-gel layer. Hence the amount of Cu deposited ultimately determined the diameter of the VLS-grown Si microwire. If too little copper was deposited, when the wafer was heated to 1000˚C, the Cu separated into multiple wire nucleation sites, allowing multiple wires to grow out of each hole. The hole diameter also limited the final wire diameter, because the maximum wire diameter is highly correlated with the diameter of the holes. Once the Cu electrodeposition was complete, the electrodeposition solution was pipetted out of the cell, and the wafer was gently rinsed and dried under a stream of N_2(g).

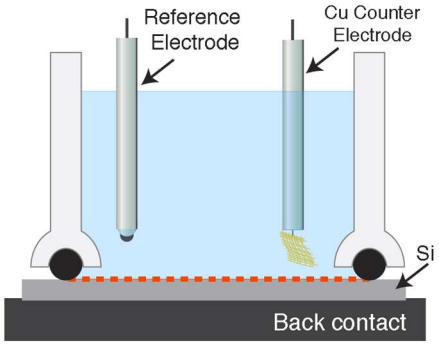

Figure S1: Schematic of the copper electrodeposition cell.

Microwire Growth: After electrodeposition of Cu, the Si substrate wafer was cleaved into chips ~ 1.5 cm x 3 cm in size. The chips were rinsed with isopropanol and then thoroughly dried in a stream of N_2(g). Each chip was placed in a quartz tube in a chemical vapor deposition system, and exposed to vacuum for 30 min to remove oxygen and any adsorbed gases. The sample was then heated to 1000 ˚C under He and annealed for 20 min at ~750 torr under a 500 sccm flow of H_2(g). Si MWs were grown using 450 sccm of H_2, 50 sccm of $SiCl_4$ and 1.3 sccm of BCl_3 (to create p-type microwires), with a growth time of 8 – 20 min, depending on the

desired microwire length. The sample was cooled under H_2 to 750˚C over the course of 5 min, and was then cooled to room temperature (under ~750 torr of He) over the course of 20 min.

Array Processing: Prior to electrochemical testing, the wire arrays were cleaned, processed and made into electrodes using an RCA2 (5:1:1 H_2O:HCl:30% H_2O_2 at 70 ˚C) cleaning procedure that has been reported elsewhere.[2-3] To create a protective boot at the base of the wires, a dry thermal ~150 nm thick oxide was grown at 1100˚C over the entire array (**Figure S2**). The oxide-coated arrays were then infilled with a mixture of 10:1 Sylgard 184 PDMS mixed 1:3 (v:v) with toluene (Sigma), to protect the oxide at the base of the microwires. This mixture had a sufficiently low viscosity to spin into the Si MW arrays and thereby produce a ~ 20 μm thick infill layer. The arrays were then briefly etched in a 3:1 (v:v) solution of 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99.5%):*tert*-butyl ammonium fluoride (Sigma-Aldrich, 75 wt% in water) to remove any PDMS from the wire tops, and were then etched for ~3 min in buffered HF(aq) (Transene, Inc.) to remove the thermal oxide from the tops of the wires. To remove the PDMS infill, the samples were etched for >30 min in the same 3:1 solution of 1-methyl-2pyrrolidinone:tert-butyl ammonium fluoride.[4]

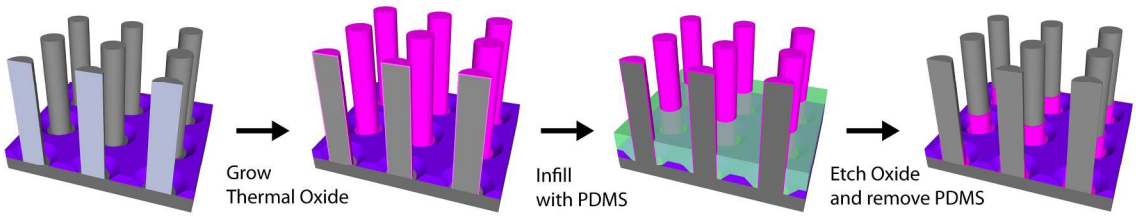

Figure S2: Scheme for creating a protective oxide "boot" on the microwires to prevent shunting through the wire bases and/or the degenerately doped substrate wafer.

Characterization: The fidelity of the patterned template was confirmed by optical microscopy, scanning electron microscopy (SEM), profilometry and atomic force microscopy (AFM). The fidelity of the microwire arrays was confirmed by SEM and the electrochemical performance was measured using a Princeton Applied Research Model 273 potentiostat.

Electrode Fabrication: Electrodes were made by breaking the substrates coated with Si wire arrays into chips that had areas between 0.01 cm^2 and 0.1 cm^2. Epoxy (Loctite 9460) was used to define the active area of the electrodes. A Ga-In eutectic was scratched into the back of the chips, to create an ohmic contact to the p^+ silicon substrate. Each chip was then attached with Ag paint to a coil of tinned Cu wire. The electrodes were sealed into glass tubes ~18 cm in length, and the back, sides and any exposed wire were covered in epoxy (Loctite 9460, Hysol 1C) to ensure that the only path for the photogenerated carriers was from the microwire sample through the insulated wire to the potentiostat. Electrode areas were determined using a scanner and image processing software (ImageJ).[5]

Photoelectrochemical Testing: To evaluate the electrical performance of the microwire arrays, the electrodes were tested in an aqueous solution of 50 mM MV^{2+}, from which the reduced MV^+ species is generated *in situ,* in a solution of 0.10 M phthalate buffer and 0.40 M potassium sulfate (adjusted to pH = 3.0). The electrochemical cell was illuminated from the bottom using an 808 nm diode laser at 60 mW cm^{-2}. A Pt counter electrode and the SCE were used to determine the limiting current densities in the oxidized methyl viologen solution, and the carbon cloth counter electrode and reference electrode were used during the collection of the current density vs potential (*J-E*) data in the solution that contained the reduced form of the redox species, $MV^{+\cdot}$.

The light intensity was monitored by placement of a calibrated Si photodiode next to the working electrode. To minimize mass transport effects, rapid stirring was used during all electrochemical measurements of the properties of Si MW arrays.

The spectral response system consisted of a 150 W Xe lamp and a monochromator (Oriel), along with a potentiostat (Gamry Series G 300) and a 30 Hz chopper.[5] The electrodes were immersed in the $MV^{2+/+}$ redox couple (50 mM), and the working electrode was poised at -0.50 V vs. SCE. A beam splitter and reference photodiode provided a continuous measurement of the monochromator output light intensity. The potentiostat measured both the current from the Si MW working electrode and from the reference photodiode. The data were then analyzed to compute an external quantum yield for each wavelength, and thereby to determine the spectral response characteristics of the microwire arrays.

Analysis of J-E Data in Methyl Viologen Redox Solutions

The potential data were corrected for iR losses using:[5-6]

$$V_{corr} = V - iR_{cell} - \eta_{conc} \qquad (1)$$

where the correction for the concentration overpotential (η_{conc}) was performed using:[5-6]

$$\eta_{conc} = \frac{k_B T}{nq}\left[\ln\left(\frac{J_{l,a}}{-J_{l,c}}\right) - \ln\left(\frac{J_{l,a}-J}{J-J_{l,c}}\right)\right] \qquad (2)$$

In **Equation (2)**, k_B is Boltzmann's constant, T is the absolute temperature, n is the number of moles of electrons transferred, q is the unsigned charge on an electron, $J_{l,a}$ is the limiting anodic current density, and $J_{l,c}$ is the limiting cathodic current density. To determine the limiting anodic and cathodic current densities, a glassy carbon working electrode was used, and *J-E* data (with a carbon cloth reference electrode and a carbon cloth counter electrode) were taken from 0.00 V to -0.40 V to +0.20 V vs. the carbon cloth reference electrode.[5] The data were corrected according

to Equation (2), with the slope of the corrected voltage data yielding a value for R_{cell}. To ensure that the data were not overcorrected, data were also collected from a planar p-Si wafer sample, and the corrections were first applied to the planar sample. The *J-E* data from the wire array electrodes were then corrected using **Equation (1)**, and the figures of merit for each electrode were extracted from the corrected data.

Planar p-Si Controls: To ensure the validity of the Si MW data, a planar p-Si (R = 0.6-0.8 Ω-cm) electrode was also tested in contact with the methyl viologen redox species for both *J-E* **(Figure S3)** and spectral response measurements. The higher overall current density of the planar sample makes it harder to get the highly absorbing MV^+ away from the electrode. Thus, the jaggedness of the planar curves is due to stirring and mass transport effects. The figures of merit for this electrode were V_{oc} = 540 ± 10 mV, J_{sc} = 20 ± 3 mA cm^{-2}, $\Phi_{ext,sc}$ = 0.51 ± 0.00, *ff* = 0.74 ± 0.04 and η_{808} = 13 ± 2%.

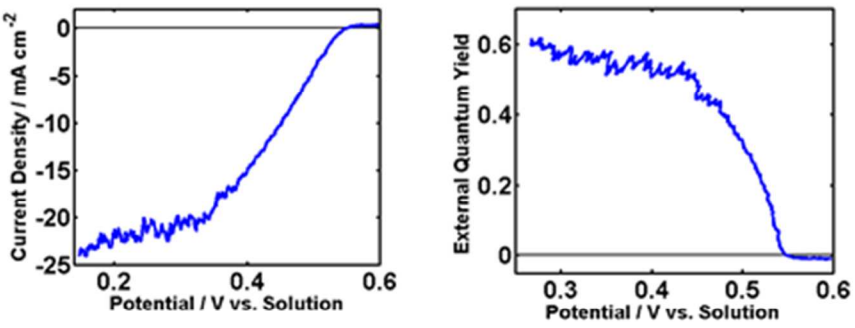

Figure S3: *J-E* data and external quantum yield for planar p-Si measured in aqueous methyl viologen electrolyte.

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